

Suppression of Quantum Phase Interference in Molecular Magnets Fe_8 with Dipolar-Dipolar Interaction

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Renormalized tunnel splitting with a finite distribution in the biaxial spin model for molecular magnets is obtained by taking into account the dipolar interaction of environmental spins. Oscillation of the resonant tunnel splitting with a transverse magnetic field along the hard axis is smeared by the finite distribution which subsequently affects the quantum steps of hysteresis curve evaluated in terms of the modified Landau-Zener model of spin flipping induced by the sweeping field. We conclude that the dipolar-dipolar interaction drives decoherence of quantum tunnelling in molecular magnets Fe_8 , which explains why the quenching points of tunnel splitting between odd and even resonant tunnelling predicted theoretically were not observed experimentally.

Macroscopic quantum phenomena in magnetic molecular clusters have been being an attractive field in recent years[1, 2, 3, 4, 5, 6, 7, 8]. Octanuclear iron(III) oxo-hydroxo cluster Fe_8 is of special interest because it shows not only regular steps in hysteresis curve but also oscillation of the tunnel splitting due to the quantum phase interference [3]. Oscillation of tunnel splitting of the ground state with respect to the external field along the hard axis was predicted theoretically by Garg [4] as a consequence of the quantum phase interference of tunnel paths, and it was subsequently generalized to tunnelling at excited states and resonant tunnelling for quantum transition between different quantum states with its x component of the spin $S_x = -10$ and $10 - n$ (along the easy axis of Fe_8) recently [6]. The quenching points between even and odd n have a shift $\pi/2$. However, a serious problem, why the theoretically predicted shift of quenching points of tunnel splitting between odd and even resonant tunnelling was not observed in the experimental hysteresis curves [3,6,9], remains to be solved. This is the main motivation of this Letter. Here we use the Landau-Zener model [3,8,9,10] to describe the spin flipping induced by the sweeping field with a modified bare tunnel splitting considering the dipolar interaction with environmental spins. There are two basic interactions to be considered: spin-phonon and spin-spin interactions. For the molecular magnets Fe_8 in mK temperature region, the spin-phonon interaction [8] can be safely ignored as the spin-lattice relaxation time is extremely long [11]. The interaction between the big spin and the environmental spins was considered as the main source of decoherence of tunnelling in magnetic macromolecules [12] and recently it was shown that the nuclear spin plays an important role in magnetic relaxation [13,14]. In this Letter, starting from the mean field approximation, the dipolar interaction is treated as a local stray field \vec{h} (see the following) with a Gaussian distribution. The tunnel splitting in the Landau-Zener transition rate should be

considered as an average over the local stray field \vec{h} . In doing so we find that the quenching of the tunnelling due to quantum interference is suppressed by the local stray field, and the steps in the hysteresis curve corresponding to odd resonant tunnelling are understood.

We start with the biaxial spin model for the molecular magnets Fe_8 [3-5]. The Hamiltonian is given by [15]

$$H = K_1 S_z^2 + K_2 S_y^2 - g\mu_B \mathbf{S} \cdot (\mathbf{B} + \vec{h}), \quad (1)$$

where $K_1 > K_2 > 0$ and \mathbf{B} is the external magnetic field. The term $-g\mu_B \mathbf{S} \cdot \vec{h}$ is the dipolar-dipolar interaction between the magnetic molecular cluster and the environmental spins, i.e. $\vec{h} = \sum_j J_{ij} \mathbf{S}_j$, where the summation runs over the neighboring clusters. Strictly speaking, this should be a many-body problem. In this Letter, \vec{h} is treated approximately as a local stray field, $\vec{h} = \sum_j J_{ij} \langle \mathbf{S}_j \rangle$. Both experimental [14] and the Monte Carlo study[16,17] show that \vec{h} has a random distribution with a distribution width in proportion to $(1 - |M|)$ and its mean value proportional to M where M is the total magnetization of the system. Here we assume that \vec{h} has a Gaussian distribution with an equal distribution width in all directions [18]

$$P(\vec{h}) = \frac{1}{(2\pi\sigma^2)^{3/2}} \exp \left[-(\vec{h} - \vec{h}_0)^2 / 2\sigma^2 \right]. \quad (2)$$

To simulate the experimental setup [3], the external magnetic field is taken to be $\mathbf{B} = \{B_x, 0, B_z\}$: a uniform field B_z along the hard axis and the sweeping field B_x on the easy axis $B_x = n\Delta B \pm ct$ where n is integer, ΔB is the field interval between neighboring resonant tunnelling and $c = dB_x/dt$. In the following calculation, we take $K_1 = 0.310\text{K}$, $K_2 = 0.229\text{K}$, and $c = 0.1\text{T/sec}$ for the molecular magnets Fe_8 [3].

Theoretically, quantum tunnelling for a spin system without the local stray field can be understood in the instanton method [4-6], the Landau-Zener model [8-10],

and by diagonalizing the Hamiltonian numerically [3, 19]. The instanton method can give the tunnel splitting. When the field along the easy axis satisfies the resonant condition, $B_x + h_x = n\Delta B$, the transition rate, while the field on the easy axis sweeps over the resonant point, is given by the Landau-Zener transition formula [8-10], $P_{LZ} = 1 - \exp(-\pi\Delta_n^2/\nu_n)$, where Δ_n is the tunnel splitting and $\nu_n = 2g\mu_B\hbar(2s-n)c$. It should be noted that in this way we have assumed tacitly that the tunnel splitting for all the spins inside the resonant window are the *same* and thus all the spins tunnel with the *same* transition rate. However, when the local stray field due to the dipolar-dipolar interaction is taken into account, such a picture should be modified. A random distribution of local stray fields like Eq.(2) with a distribution width $\sigma \sim 0.05\text{T}$ typical for the molecular magnets Fe_8 will block the resonant tunnelling of either the ground state or the low-lying excited states [13]. Nevertheless, such a problem can be circumvented by using the sweeping field along the easy field. When B_x sweeps over the resonant point, it will make the spins with different h_x 's to satisfy the resonant condition, and allows continuous relaxation. Since the tunnel splitting is very sensitive to the transverse local fields $B_z + h_z$, and h_y [4-6], the spins tunnel with *different* tunnel splitting while B_x is sweeping over the resonant point. Consequently, the spin transition rate observed in the experiment should be given by

$$\langle P_{LZ} \rangle \simeq 1 - \exp\{-\pi \langle \Delta_n^2 \rangle / \nu_n\}, \quad (3)$$

where $\langle \cdots \rangle$ represents the average over the distribution of the local stray field, i.e., $\langle \Delta_n^2 \rangle = \int \Delta_n^2(\vec{h}) p(\vec{h}) d\vec{h}$. Accordingly, the tunnel splitting extracted from the measured transition rate should be $\sqrt{\langle \Delta_n^2 \rangle}$ but not Δ_n . In other words, the starting point to understand the experimental observation should be $\sqrt{\langle \Delta_n^2 \rangle}$ instead of Δ_n . The two quantities are qualitatively different from each other as we shall show in the following.

The instanton method [4-6] is efficient and powerful to evaluate the tunnel splitting Δ_n . The Lagrangian for the biaxial model Eq.(1) is

$$L(\mathbf{n}) = -s\hbar(1 - \cos\theta)\dot{\phi} - \langle \mathbf{n} | H | \mathbf{n} \rangle, \quad (4)$$

where $|\mathbf{n}\rangle$ is the spin coherent state. With the help of the mapping technique, $(\phi, p = s\hbar\cos\theta)$ is regarded as a pair of canonical variables. To calculate the excited state tunnelling or resonant tunnelling, one needs to apply the Bohr-Sommerfeld quantization rule $\oint p d\phi = n\hbar$ to define the classical orbits (n is an integer). Then a propagator with both imaginary and real time will be used to describe the tunnelling between two degenerate states,

$$K(n_f, T/2; n_i, -T/2) = \langle n_f | e^{iHT/\hbar} | n_i \rangle \\ = \int d\Omega \exp \left[\frac{i}{\hbar} \int_{-T/2}^{T/2} L(\mathbf{n}) dt \right]. \quad (5)$$

The tunnel splitting is found by integrating over two degenerate classical orbits. In molecular magnets Fe_8 the local stray field is rather weak, i.e. $g\mu_B|\vec{h}|/(K_2s) \ll 1$. We calculate the tunnel splitting at the n th resonant tunnelling point with the transverse field $B_z + h_z$, and h_y , and obtain that,

$$\Delta_n \approx \frac{Q_n}{2} e^{-S_c^n} \{ |e^{2qh_y} + e^{-2qh_y} + 2\cos[2(s\pi - n\pi/2 - d_n h_z - d_n B_z)]| \}^{1/2}, \quad (6)$$

where and S_c^n is the instanton action

$$S_c^n = \int_0^{\pi-\phi_n} d\phi \sqrt{\frac{V(\phi) - E_n}{K_1(1 - \lambda \sin^2 \phi) + (g\mu_B n \Delta h/s) \cos \phi}}, \quad (7)$$

$$V(\phi) = K_2 s^2 \sin^2 \phi - g\mu_B n \Delta h s \cos \phi \\ - \frac{[g\mu_B(h_z + B_z)]^2}{2K_1(1 - \lambda \sin^2 \phi) + 2(g\mu_B n \Delta h/s) \cos \phi}, \quad (8)$$

E_n is the energy of the n th excited state, ϕ_n is the turning point determined by $V(\pi - \phi_n) = E_n$, Q_n is the pre-factor

$$Q_n \simeq 4\pi / \sqrt{V''(0)(2K_1 + g\mu_B n \Delta h/s)}, \quad (9)$$

$q = g\mu_B \pi \lambda^{1/2} / 2K_2(1 - \lambda)^{1/2}$, $\lambda = K_2/K_1$, and

$$d_n = \frac{g\mu_B}{2K_1} \int_0^\pi \frac{d\phi}{1 - \sin^2 \phi - \frac{g\mu_B}{2K_2 s} n \Delta h \cos \phi}. \quad (10)$$

Using the parameters in Fe_8 , it is found that the contribution from h_y and h_z to S_c^n and thus $Q_n e^{-S_c^n}$ is very small under the condition $g\mu_B|\vec{h}|/(K_2s) \ll 1$. The average value of Δ_n^2 is given by

$$\langle \Delta_n^2 \rangle \approx \frac{Q_n^2}{4} e^{-2S_{c0}^n} \left\{ e^{2q^2\sigma^2} (e^{2qh_0} + e^{-2qh_0}) + 2e^{-2d_n^2\sigma^2} \cos[2(s\pi - n\pi/2 - d_n h_0 - d_n B_z)] \right\}. \quad (11)$$

where $Q_{n0} = Q_n(h_z = h_y = 0)$, $S_{c0}^n = S_c^n(h_z = h_y = 0)$. In the absence of the stray field, i.e. $\sigma = h_0 = 0$, the above expression reduces to

$$\sqrt{\langle \Delta_n^2 \rangle} \Big|_{\sigma=h_0=0} = \Delta_n(h_x = h_y = 0) \\ = Q_{n0} e^{-S_{c0}^n} |\cos(s\pi - n\pi/2 - d_n B_z)|, \quad (12)$$

which indicates the oscillation of the tunnel splitting with the transverse field and a shift $\pi/2$ of quenching point between the odd and even resonant tunnelling, recovering the results in the previous works [3-6]. This is known as a result of the quantum interference of the tunnelling along two different paths. Qualitative difference between $\sqrt{\langle \Delta_n^2 \rangle}$ and $\Delta_n(h_x = h_y = 0)$ can now be seen by comparing Eq.(12) with Eq.(11). In the case of $B_z = 0$ and integer spin, Eq.(12) predicts that odd n resonant tunnelling quenches due to the quantum interference, while

in the presence of the stray field Eq.(11) gives non-zero tunnel splitting

$$\sqrt{\langle \Delta_n^2 \rangle}_q \simeq \frac{\sqrt{2}}{2} Q_{n0} e^{-S_{c0}^n} \sqrt{e^{2q^2\sigma^2} - e^{-2d_n^2\sigma^2}} \quad (13)$$

for $h_0 = 0$. The quenching due to the quantum interference is suppressed by the local stray field. In another word the quantum tunnelling for odd n is decoherenced because of the dipolar interaction with the environmental spins. The tunnel splitting of all six resonant tunnelling for the molecular magnets Fe_8 with and without the local stray field are shown in Table I. We see that $\sqrt{\langle \Delta_n^2 \rangle}$ for an odd n increases from zero while the random field become stronger. The random field also increases the tunnel splitting of even resonant tunnelling. It increases about 2.7 times as σ becomes as large as 0.08T, which resolves the puzzling that the experimental observation is about 3.0 times larger than the numerical result for the tunnel splitting [3]. A detailed evolution of the tunnel splitting with the distribution width around the topological quenching points is shown in Fig.1. As the width of the distribution is proportional to $(1 - |M|)$, the calculated results for different M are shown in Fig.1, which are in good agreement with the experimental observation (see Fig.10 in Ref.[20]). One can see from Eq.(11) that the main effect of h_0 is to provide an initial phase and thus shifts the oscillation. For Fe_8 , $h_0 \simeq \sigma/4$ [16], and the effect of modification for nonzero h_0 is almost omissible.

Table I: Tunnel splitting $\sqrt{\langle \Delta_n^2 \rangle}$ (the unit is Kelvin) for Fe_8 in the case of $B_z = h_0 = 0$.

n	$\sigma = 0.0\text{T}$	$\sigma = 0.02\text{T}$	$\sigma = 0.05\text{T}$	$\sigma = 0.08\text{T}$
0	8.399×10^{-10}	8.547×10^{-10}	1.087×10^{-9}	2.312×10^{-9}
1	0.0	2.459×10^{-9}	3.266×10^{-9}	6.450×10^{-9}
2	3.414×10^{-8}	3.473×10^{-8}	4.418×10^{-8}	9.393×10^{-8}
3	0.0	2.399×10^{-7}	3.187×10^{-7}	6.293×10^{-7}
4	2.015×10^{-6}	2.050×10^{-6}	2.608×10^{-6}	5.544×10^{-6}
5	0.0	9.878×10^{-6}	1.312×10^{-5}	2.591×10^{-5}
6	6.224×10^{-5}	6.333×10^{-5}	8.055×10^{-5}	1.713×10^{-4}

The oscillation of the tunnel splitting for $s = 10$ with various distribution width σ 's is shown in Fig.2. From Fig.2, it is shown that the oscillation of the tunnel splitting due to quantum interference is suppressed by the local stray field \vec{h} . For a distribution width $\sigma = 0.05\text{T}$ which is estimated for Fe_8 [9,13], the oscillation of tunnel splitting with respect to the field along the hard axis is still visible, while the oscillation is suppressed completely for the width as large as 0.08T. In fact, when the distribution width approaches the half oscillation period, the oscillation due to quantum interference disappears and the classical behavior, i.e. tunnel splitting increases monotonously with B_z , is resumed. The above analysis leads to a decoherence mechanism for quantum interfer-

FIG. 1: Illustration of $\sqrt{\langle \Delta_n^2 \rangle}$ ($n = 0, 1$) around topological quenching points due to quantum interference with different distribution width σ 's.

FIG. 2: The oscillation of $\sqrt{\langle \Delta_0^2 \rangle}$ with different distribution width σ 's for $s=10$. From top to bottom: $\sigma = 0.08\text{T}$, 0.05T, 0.02T, and 0.0T.

ence due to the dipolar-dipolar interactions between the spins without dissipation [12].

The magnetization jump from the spin flipping at the resonant tunnelling can be calculated from the modified Landau-Zener transition rate given in Eq.(3). In principle the time evolution of the spin system in Eq.(1) can be obtained by solving the time-dependent Schrödinger equation $i\hbar \frac{\partial}{\partial t} |\Phi\rangle = H |\Phi\rangle$, which contains a set of $(2s+1)$ coupled differential equations for the model in Eq. (1). It was shown [19] that the coupled differential equations can be reduced to that of an effective two-level system with the effective Hamiltonian. Here we have

$$H_{\text{eff}}(t) = \begin{pmatrix} -(10-n)g\mu_B ct & \sqrt{\langle \Delta_n^2 \rangle}/2 \\ \sqrt{\langle \Delta_n^2 \rangle}/2 & 10g\mu_B ct \end{pmatrix}, \quad (14)$$

near the resonant condition and the time-dependent state is given by $|\Phi_{\text{eff}}\rangle = a_{-10}(t)|-10\rangle + a_{10-n}(t)|10-n\rangle$. The tunnelling splitting in Eq.(14) is $\sqrt{\langle \Delta_n^2 \rangle}$ instead of Δ_n as

FIG. 3: Hysteresis curves with different distribution width σ 's.

we discussed. Correspondingly, the magnetization jump from the n th resonant tunnelling is obtained as

$$\Delta M_n = \langle \Phi_{\text{eff}} | S_x | \Phi_{\text{eff}} \rangle |_{t=+\infty} - \langle \Phi_{\text{eff}} | S_x | \Phi_{\text{eff}} \rangle |_{t=-\infty}. \quad (15)$$

Numerical results are shown in Fig.3. It is worth emphasizing that the resulting jump is modified as a rather smooth one due to the local stray field. The hysteresis curves in Fig.3 are drawn with the initial condition of $S_x = -10$, i.e., $a_{-10}(t = -\infty) = 1$. As it is shown in Fig. 3 the steps in hysteresis curve are smeared gradually with increasing the distribution width of the local stray field and the observed curve in experiment [3,9] can be recovered from the present theory.

In this Letter, the local stray field is treated as a “frozen” one inside the resonant window. Strictly speaking, both the width and the mean value of the distribution of the field should vary with the time-dependent magnetization during the resonant tunnelling. However, it should be noted that a “frozen” distribution is based on validity of the Landau-Zener model. If the spins “feel” the change of the local field due to spin flipping, the spin transition rate is no longer the one in Eq.(3). In that case, one should consider the non-linear Landau-Zener tunnelling [21] and the “hole-digging” mechanism [13,14]. This indicates that our result is valid when the field sweeping rate is not too small such that the evolution of the local field is relatively slower than the sweeping field. Namely, the overlap time of two levels in resonance $\tau_1 \sim \Delta_n/(2\mu_B Sc)$ should be less than the characteristic relaxation time τ_2 due to the dipolar-dipolar interaction. This means that the field sweeping rate $c > c_0 \sim \Delta_n/(2\mu_B Sc\tau_2)$. In Fe₈ [14,16] the ground state tunnelling $\Delta_0 \sim 10^{-7}$ K, $\tau_2 \sim 10^{-5}$ sec, and c_0 is estimated to be 10^{-3} T/sec., which is in good agreement with the experimental condition [3,20]. On the other hand, a finite distribution of tunnel splitting due to the local stray field has a deeper impact on the magnetic relaxation. If all the spins tunnel with the same tunnelling rate, the

magnetic relaxation should obey the exponential law, i.e. $e^{-\Gamma t}$ where $\Gamma = 2P_{LZ}c/A$ where A is amplitude of the ac field used in the experiment [20]. Instead, in the present picture, there is a finite distribution of tunnel splitting $p(\Delta_n)$ which will lead to a finite distribution of the relaxation rate $p(\Gamma)$ characteristic of the complex system like spin glass [22]. Consequently the resulting relaxation will obviously deviate from the simple exponential law as observed in the experiment [20]. Further analysis will be provided elsewhere.

We have studied the effect of dipolar interaction between giant spins in the molecular magnets Fe₈ in the mean field approximation which leads to a Zimman term of the spin in the local stray field. Our main observation is that the topological quench due to the quantum phase interference of tunnel paths is suppressed by the finite distribution of the local stray field, and the steps in the hysteresis curve corresponding to odd resonant tunnelling are explained theoretically. Thus we conclude that the dipolar-dipolar interaction leads to the decoherence of quantum tunnelling in Fe₈. Finally it is worth pointing out that the mechanism of decoherence may not be just limited in Fe₈, but can be generalized to other molecular magnets such as Mn₁₂ since the local stray field due to the dipolar-dipolar and hyperfine interactions always exists.

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